WE START WITH YES.

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ASH-DURABLE CATALYZED FILTERS FOR GASOLINE DIRECT INJECTION (GDI) ENGINES (2016 AOP LAB CALL)

June 8, 17

DOE Annual Merit Review & Peer Evaluation Meeting

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Argonne National Laboratory

DOE Project Managers: Ken Howden & Gurpreet Singh

Office of Vehicle Technologies

Project ID: ACS024

Overview

Timeline

- Start: Oct. 2015
- End: Sept. 2018
- 65% finished

Budget

- Total project funding
  - $1.5M (presumed)
- Funding received in FY16: $500K
- Funding for FY 2017
  - $500K (presumed)

Barriers

- B. Lack of cost-effective emission control
- C. Lack of modeling for combustion and emission control
- E. Durability

Partners

- Corning and Hyundai Motor Company
- University of Illinois at Urbana-Champaign
- Afton Chemical

Relevance

- GPFs are an established technology for PM reduction, in particular particulate number.
  - Targeted for stringent PM mass & number regulations (California LEVIII, U.S. Tier 3, Euro 6c & CHINA stage-6)
  - However, not much information for aging
- Information of oil-derived ash on conventional TWC is useful for TWC/GPF.
  - $CePO_4$ formation with P penetration into CeO_2 in OSC
  - It is of interest if P can react with CeO_2 in TWC coated within GPF wall (Ford, SAE 2016-01-0941 & 2017-01-0930, showed low penetration)

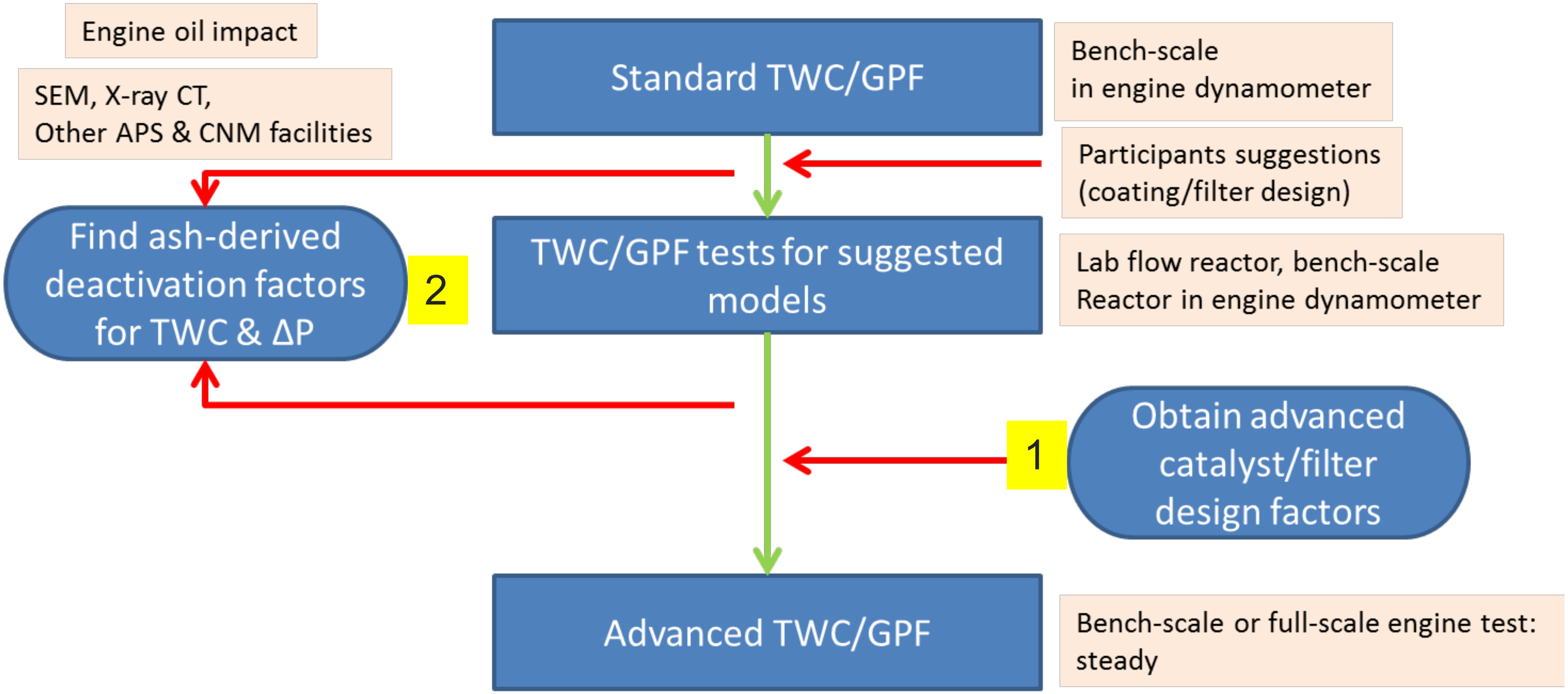
Objectives

- Objectives in FY2017
  - Understand ash formation process including ash chemistry.
  - Present oil-derived ash impacts on TWC/GPF performance and derive possible deactivation factors.
  - Add an experimental capability that enables ash loading in GPF, mimicking actual condition.

Milestones

Quarter, Year	Milestone Description	Status
Q4, 2016	Evaluate performances of fresh and aged advanced GPFs	Complete
Q1, 2017	Characterize ash distribution of ash-loaded filters using elemental mapping and X-ray tomography	On-going (aged filters will be scanned in the upcoming APS beam time)
Q2, 2017	Investigate potential catalyst deactivation mechanism by analyzing kinetics, ash chemistry and ash-catalyst interactions	On-going (new set-up added)
Q3, 2017	Design and prepare modified TWC/GPF	Complete
Q4, 2017	Conduct aging test of modified TWC/GPF	On-going

Overall Approach



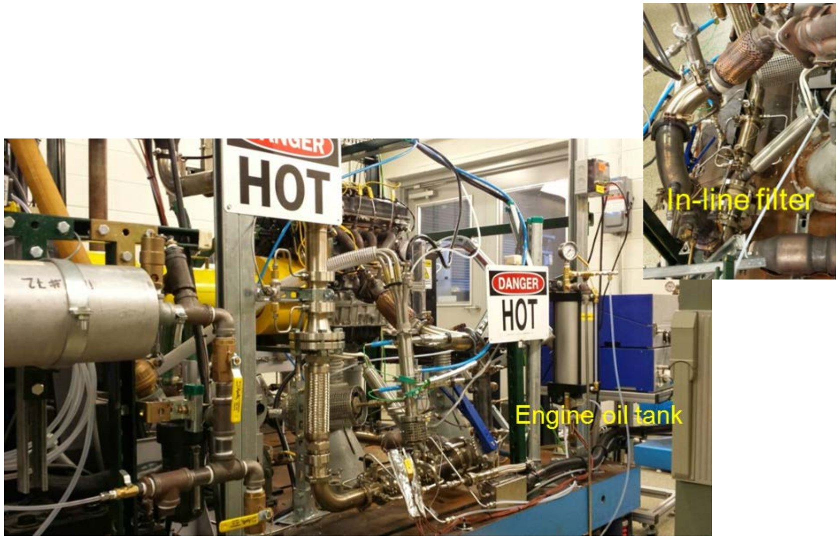
1. Project partner, Corning, limits GPF design with HP300/8 for the market.
2. Accordingly, the project team focuses more on fundamental understandings of ash properties, kinetics and others.

Approach in FY2017

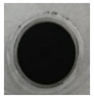
- Potential ash formation process
  - Analysis of raw ash in soot
  - Different oil formulations
  - Propose possible chemical compounds
- TWC/GPF evaluation

  → Lab-aging in a bench-scale flow reactor (single block down-sized TWC/GPFs)
  - TWC coating impacts:

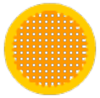
    Limited to TWC coating
- Ash-derived deactivation mechanism
  - Lab-aged & field aged GPFs
  - P penetration into wall
  - Porosity, properties of TWC

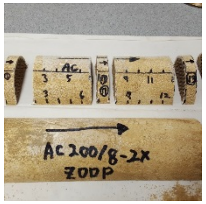


Gravimetric sampling



TEM sampling





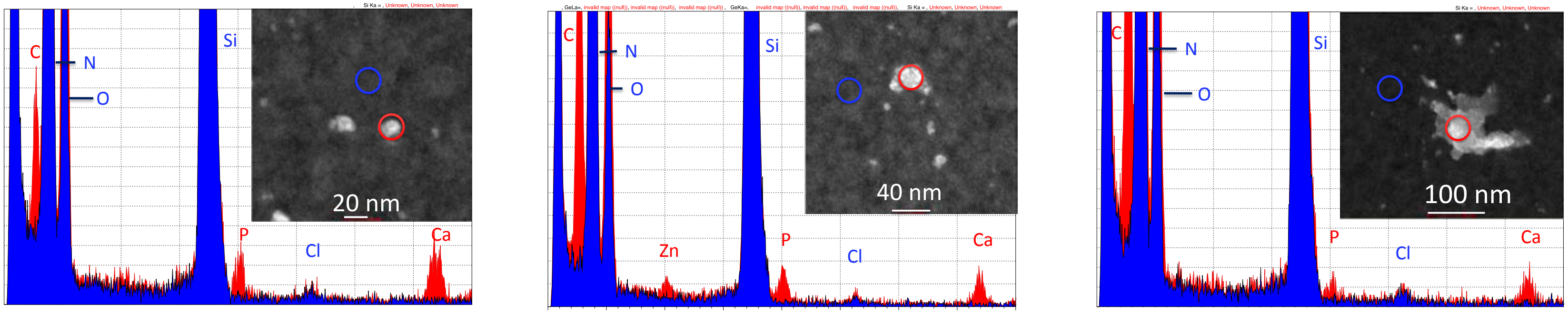
Sectioned GPFs

Characterization of GDI soot and filter substrates (APS, CNM, UIUC)

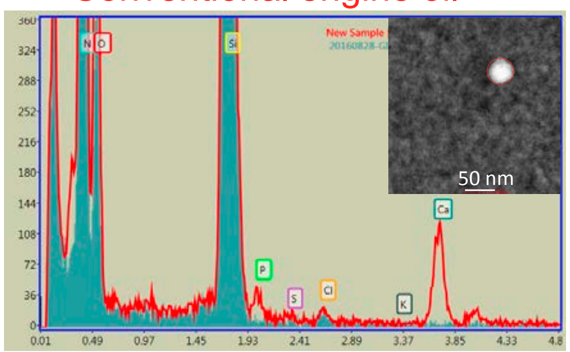
Technical Achievements in FY17

STEM-EDS showed that Ca & P are always present in any size particles, regardless of Ca/ZDDP in engine oil

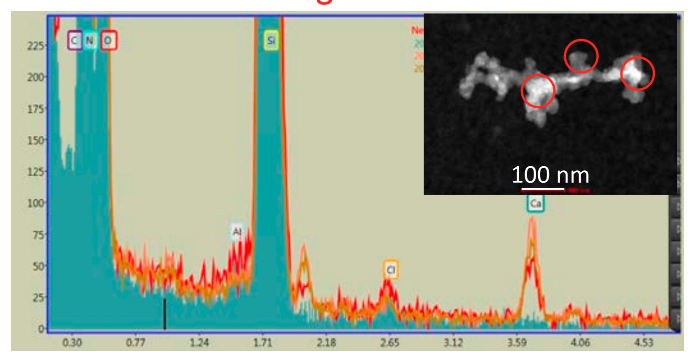
ZDDP-strengthened oil



Conventional engine oil



Ca-strengthened oil



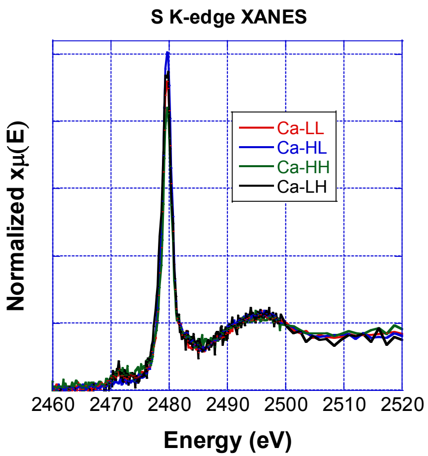
- STEM-EDS analyses were carefully performed for various sizes of ash particles collected on thin films when different types of formulated oils were dosed.
- Regardless of oil type, Ca & P were always observed. Zn presence was not always.

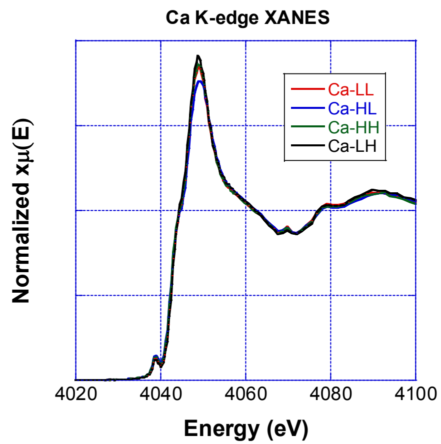
➔ No single elements of Ca, P or Zn were found.

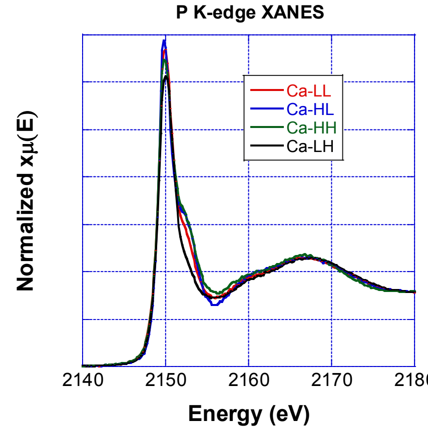
➔ Ratios of Ca to P in EDS are not identical, suggesting that these alloys are not a certain chemical compound.

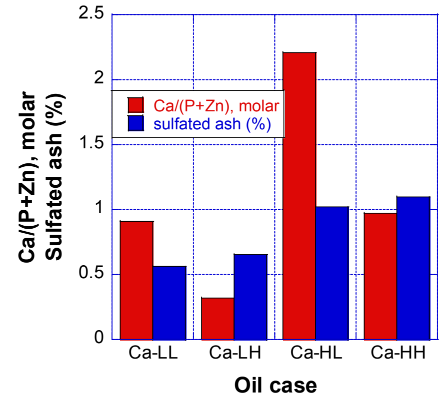
➔ Suggest early formation of complex Ca-P compounds during the combustion process.

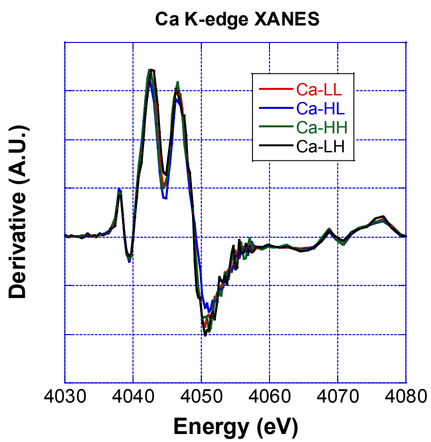
XANES proposed possible raw ash compounds present in particulates

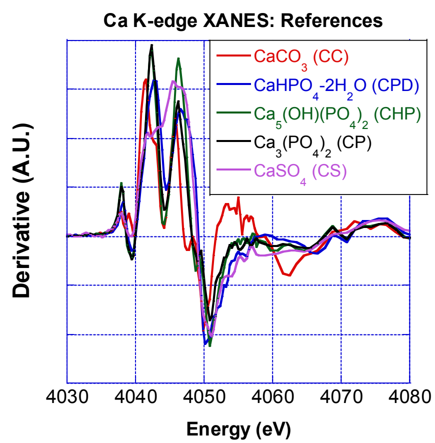


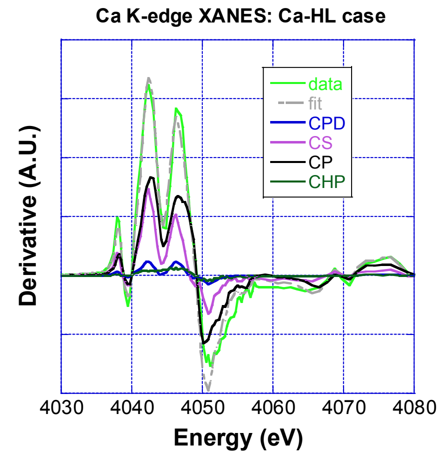


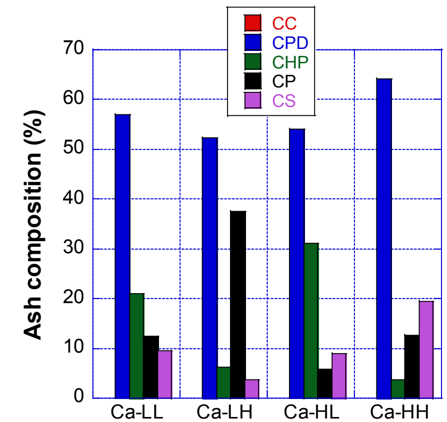






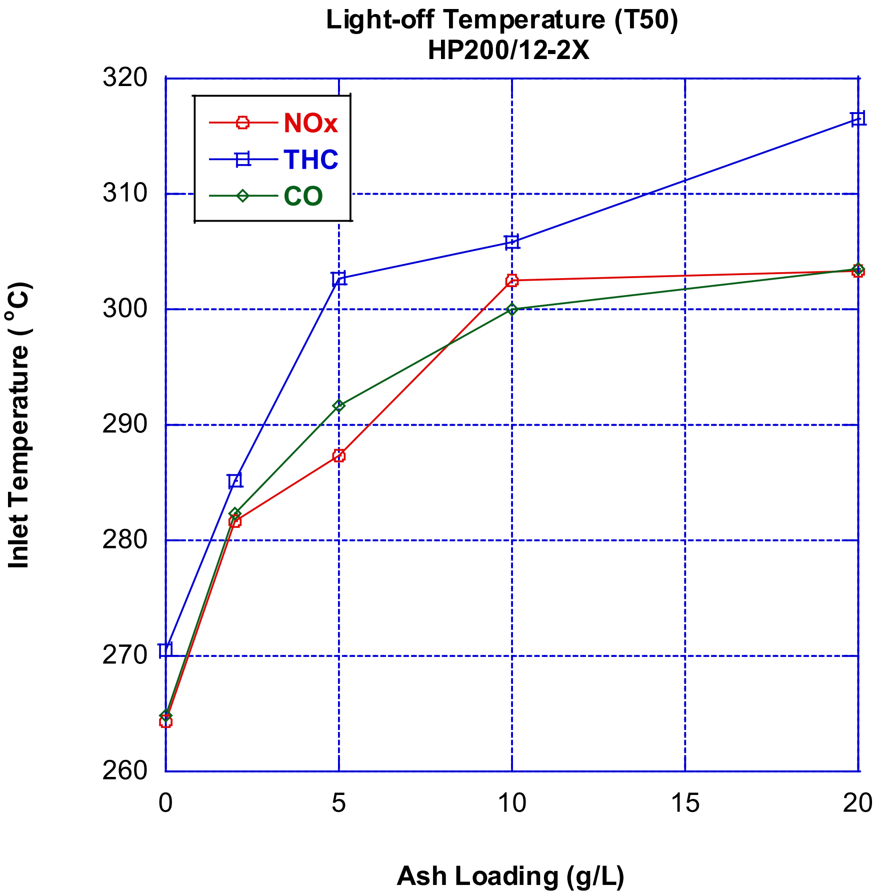


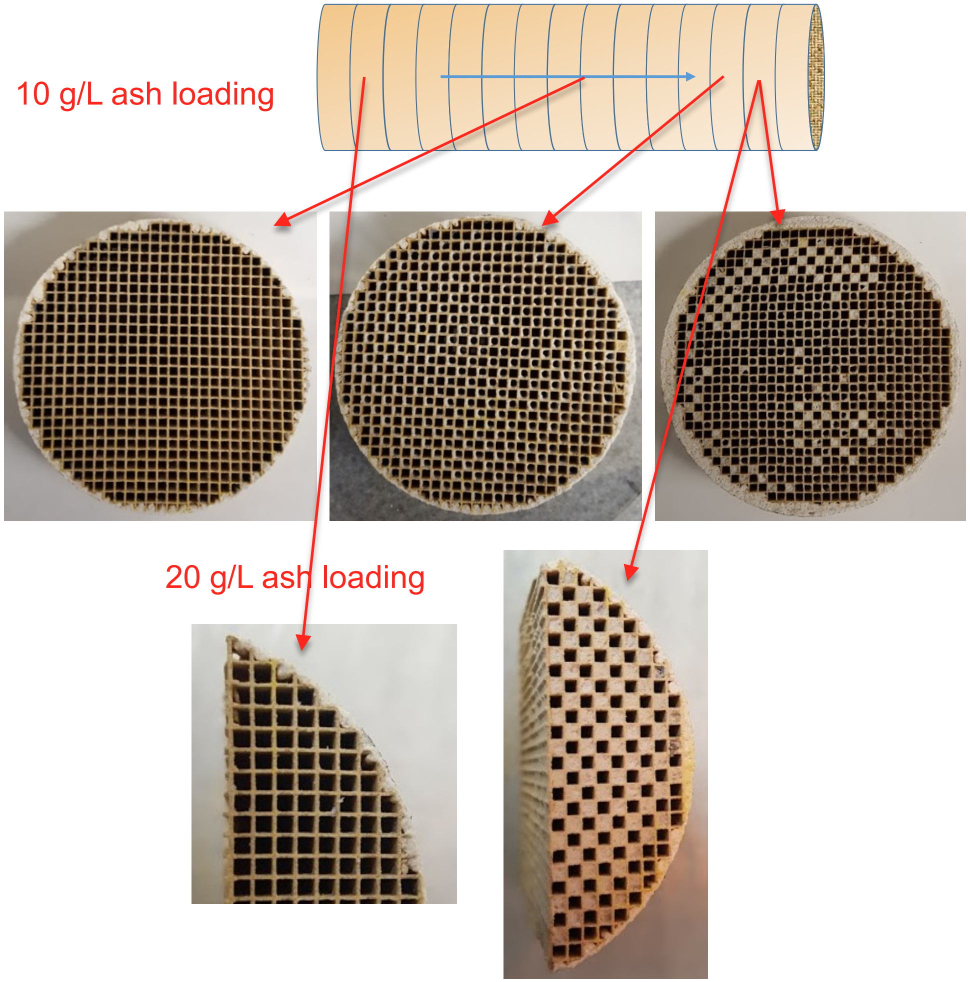




- Raw ash samples in particulates from different oil formulations (Ca & ZDDP contents) were examined for S, Ca & P K-edge XANES with reference materials.
- Limitation is present, but linear combination fitting of derivative normalized spectra suggests possible ash compounds: $ZnSO_4$, $CaHPO_4$-$2H_2O$, $Ca_5(OH)(PO_4)_2$ & $Zn_3(PO_4)$ as major contributors to sulfur, calcium & phosphorus elements.

Ash loading in TWC/GPF increased T50
Significant ash plug noted for ash loading of 20 g/L

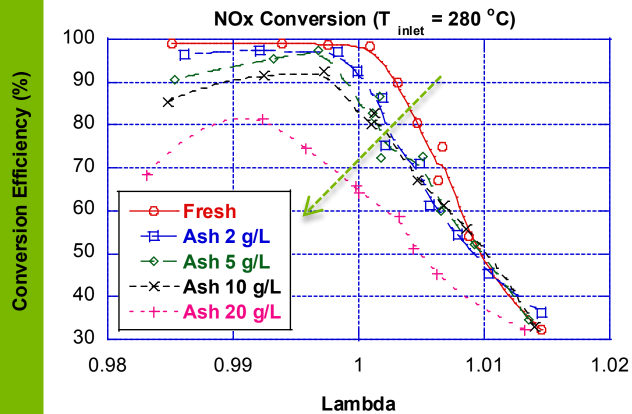


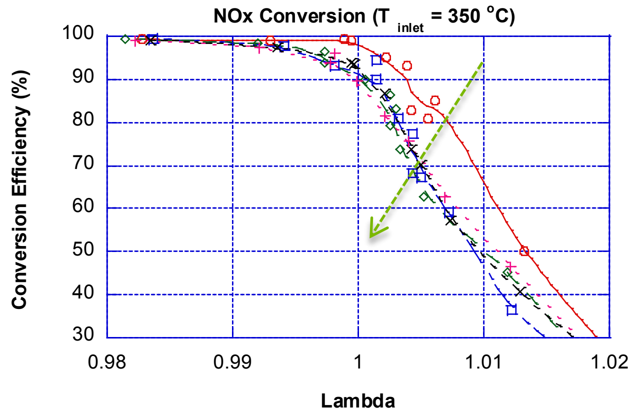


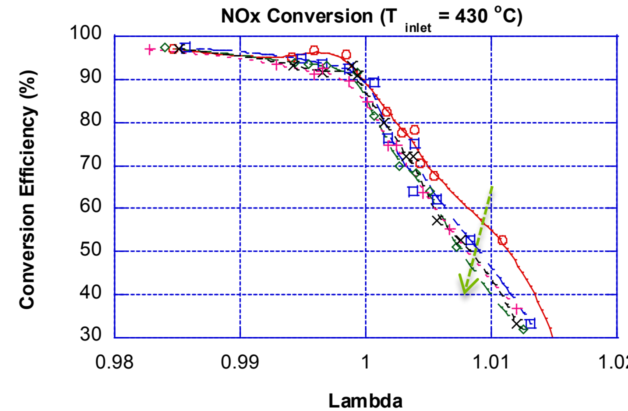
- Light-off T delay was apparent even at low ash loading (~ 5 g/L).
- Significant growth of ash plug (10 → 20 g/L) (not clear from X-ray CT in 2016 AMR)
- Lab-aging ash in filters is less compacted than in field-aged ash.

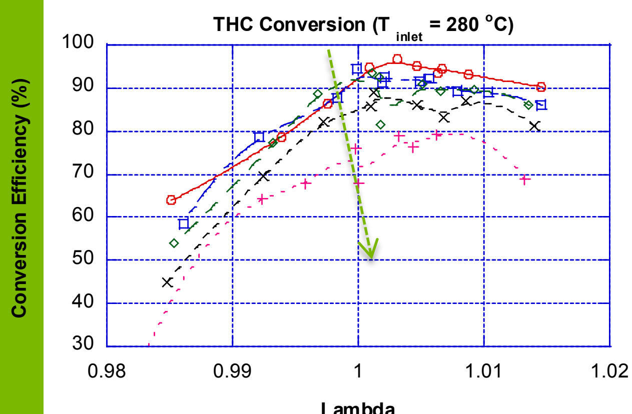
→ Possibly due to the test procedure: long active oxidation interval after soot/ash loading
→ Will address how to improve soot/ash loading condition

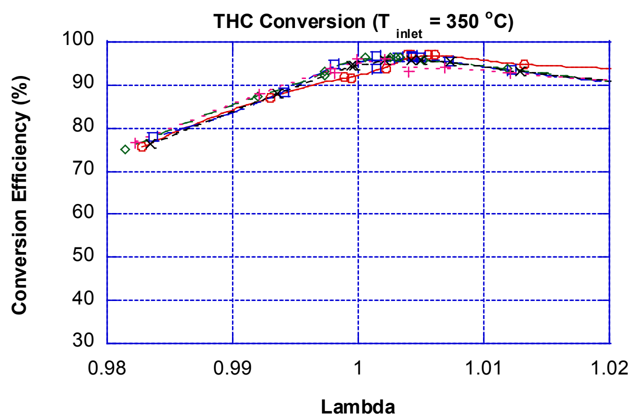
Emissions conversion efficiency with ash loading in a wide range of T and Lambda – noticeable lower performance of η_{NOx}

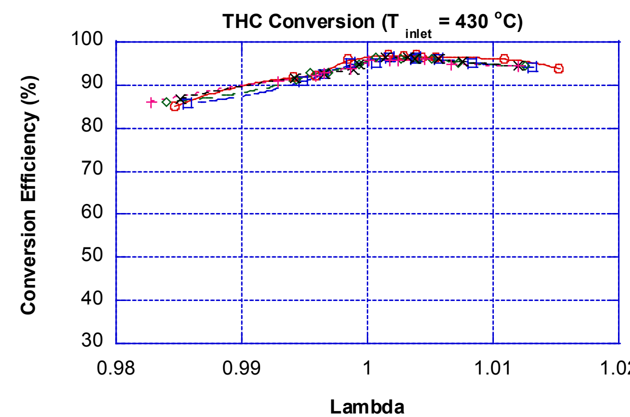


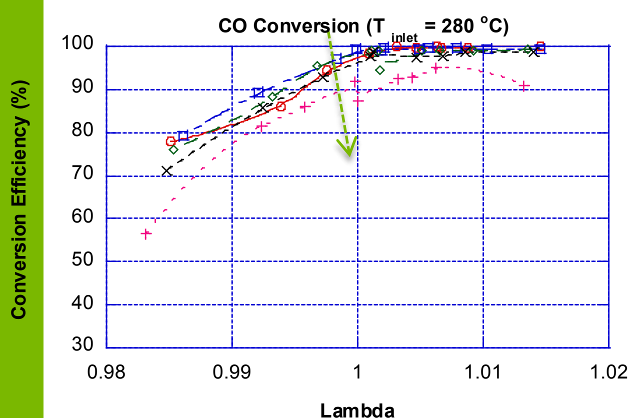








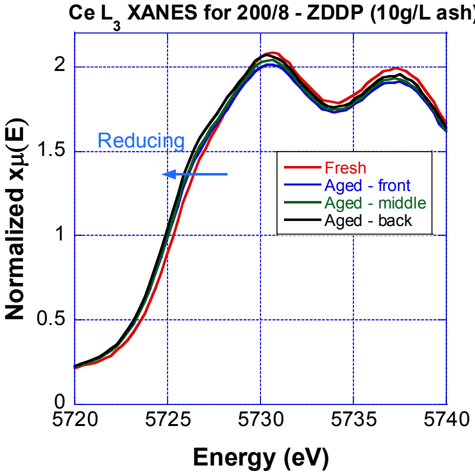


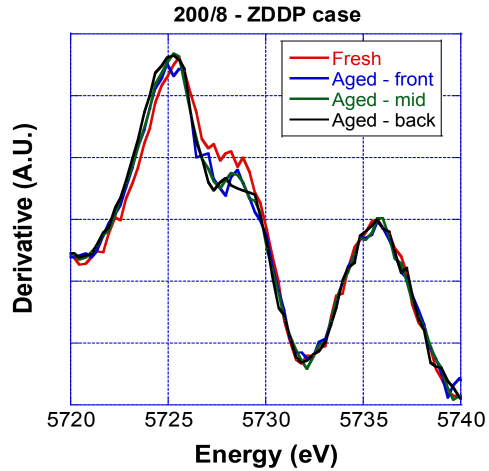


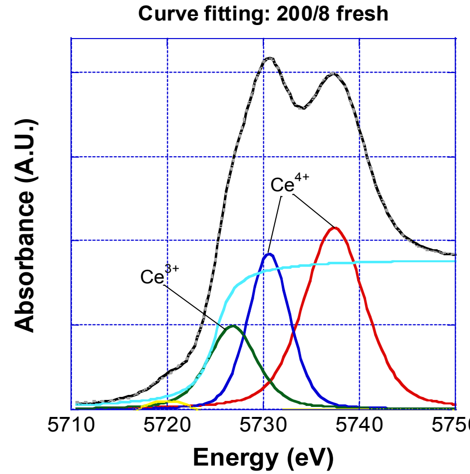
- Deactivation is more apparent under 300 °C.
- Nox is mostly impacted with ash loading, even at rich conditions.

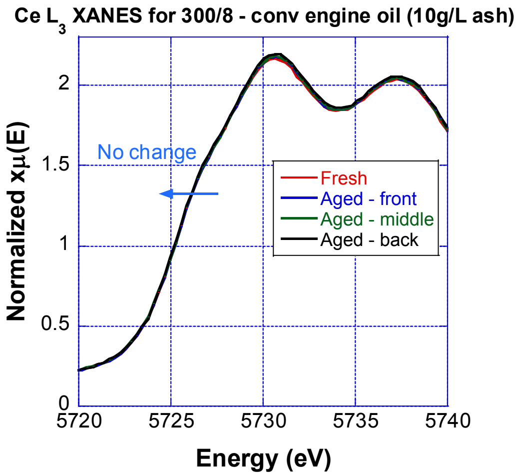
→ May hint deactivation mechanism

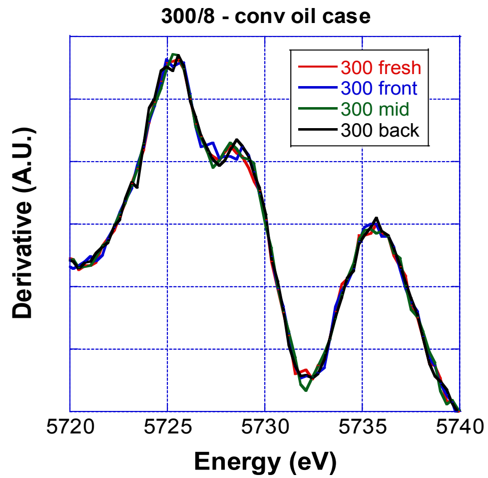
Ce in TWC was slightly reduced with ZDDP case
Field aged GPF has a trend different from lab aged GPFs

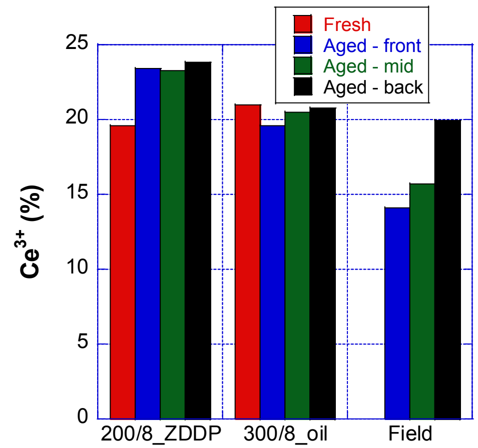






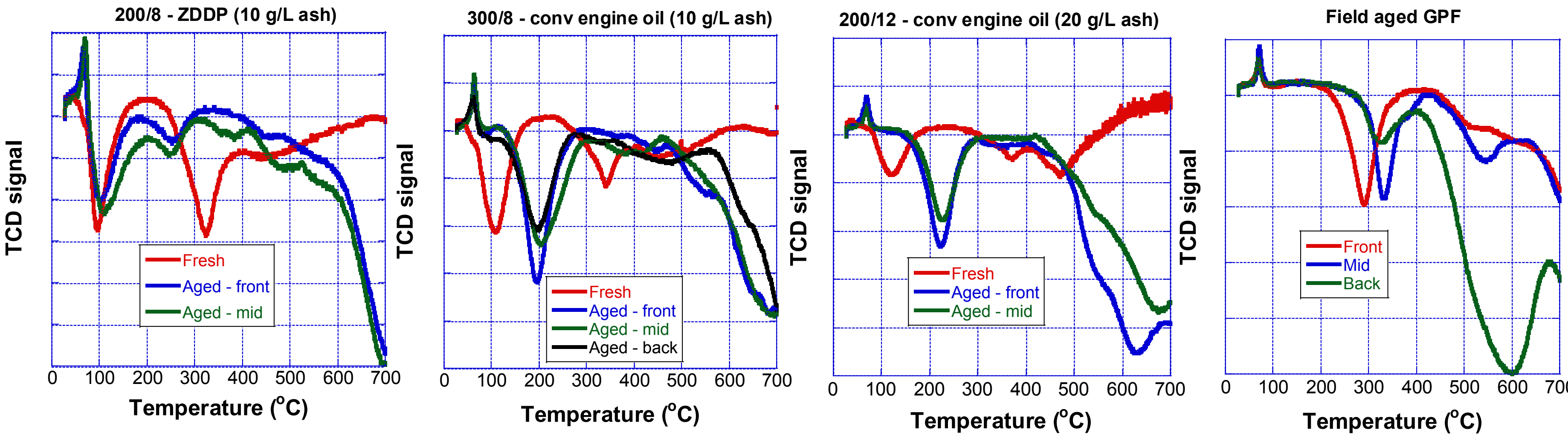






- Cerium oxidation states of TWCs in lab-aged & field-aged GPFs were examined with Ce L_3-edge XANES.
- Ce appears to slightly reduce with aging by ZDDP only based on various inspections.
- Ce in field-aged GPF is observed to reduce along the path, but no way to find Ce oxidation state in fresh filter → somehow lower reducibility: catalyst composition & temperature history

Aging conditions seem to affect reducibility of TWCs coated in GPFs



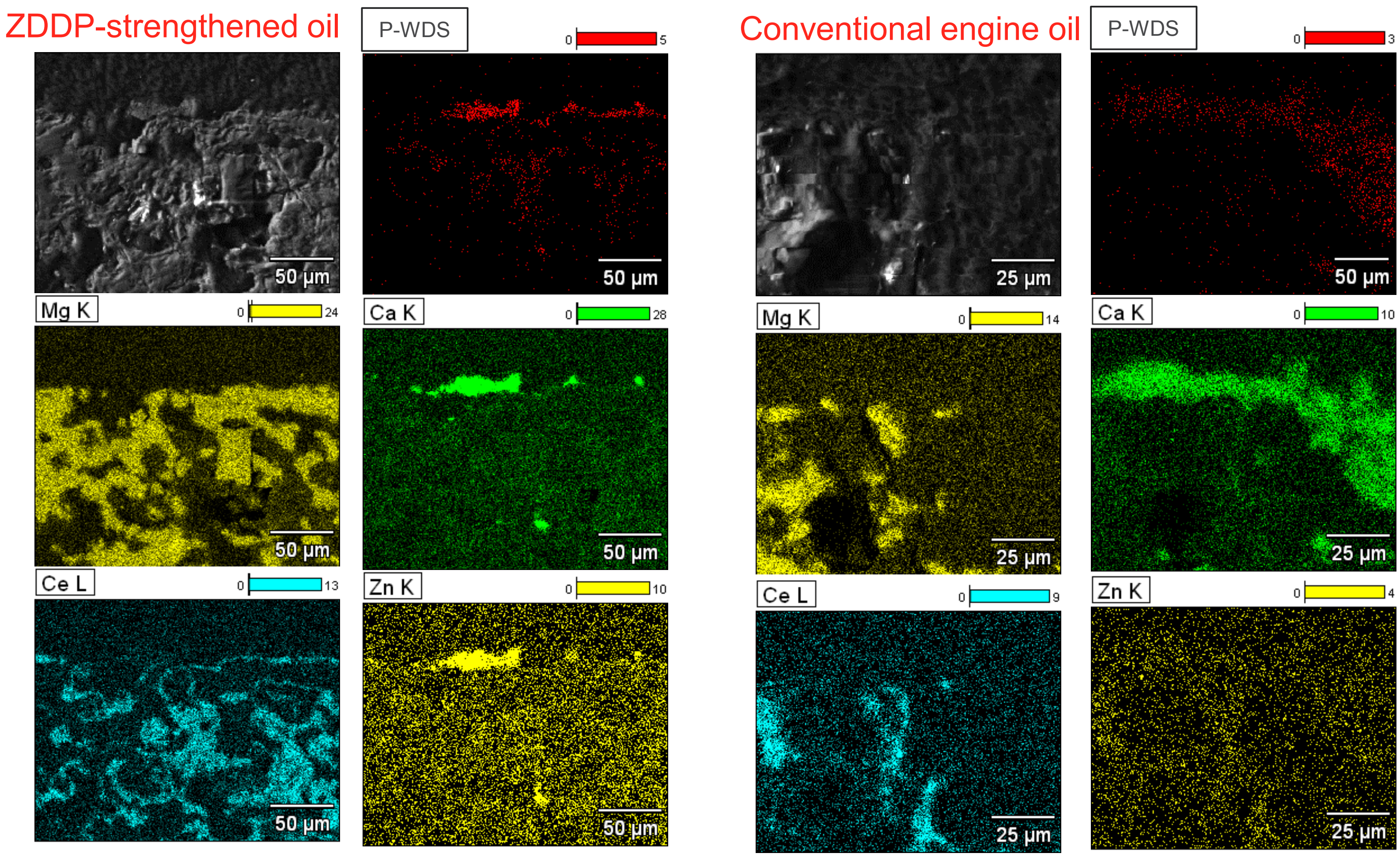
- PdOx & RhOx & their spillover to CeO_2: 50 – 200 °C, CeO_2 & Ce_x-$Zr_{1-x}O_2$: 200 – 400 °C, larger particles of OSC: T > 400 °C
- Decreased spillover & increased particle agglomeration of Pd & Rh. In comparison, PGM oxides & OSC were merged with conv. engine oil. Larger particles of OSC were noted for both oils.
- Reducing pattern of field aged GPFs is similar to that of GPFs with conv. engine oil.

→ However, reducing T of OSC is shifted to higher temperatures.

→ Increasing larger OSC particles along the path are more obvious.

→ May reflect increased impacts resulting from higher exhaust temperatures.

Low P penetration into TWC coating, in particular with conventional engine oil



- As P and Zr are not distinguished in EDS, P was analyzed with WDS. Unfortunately its intensity is low.
- P, Ca & Zn appeared mostly on the surface. P penetration was weakly observed for some filters, whose location is matched with OSC distribution with ZDDP case only.

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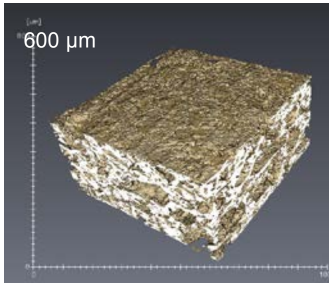
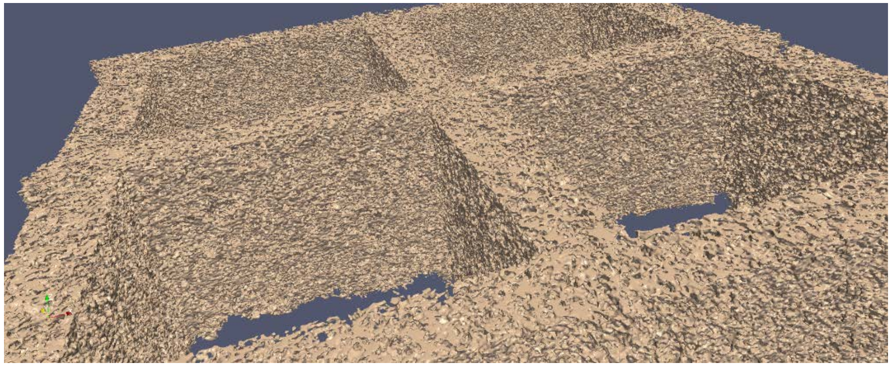
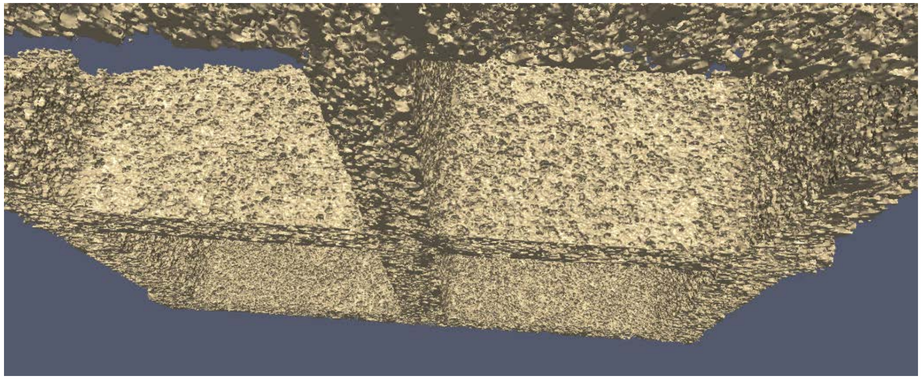
High resolution X-ray tomography images of filters were successfully obtained with bigger sizes, thanks to Dr. Powell's team



Bare filter

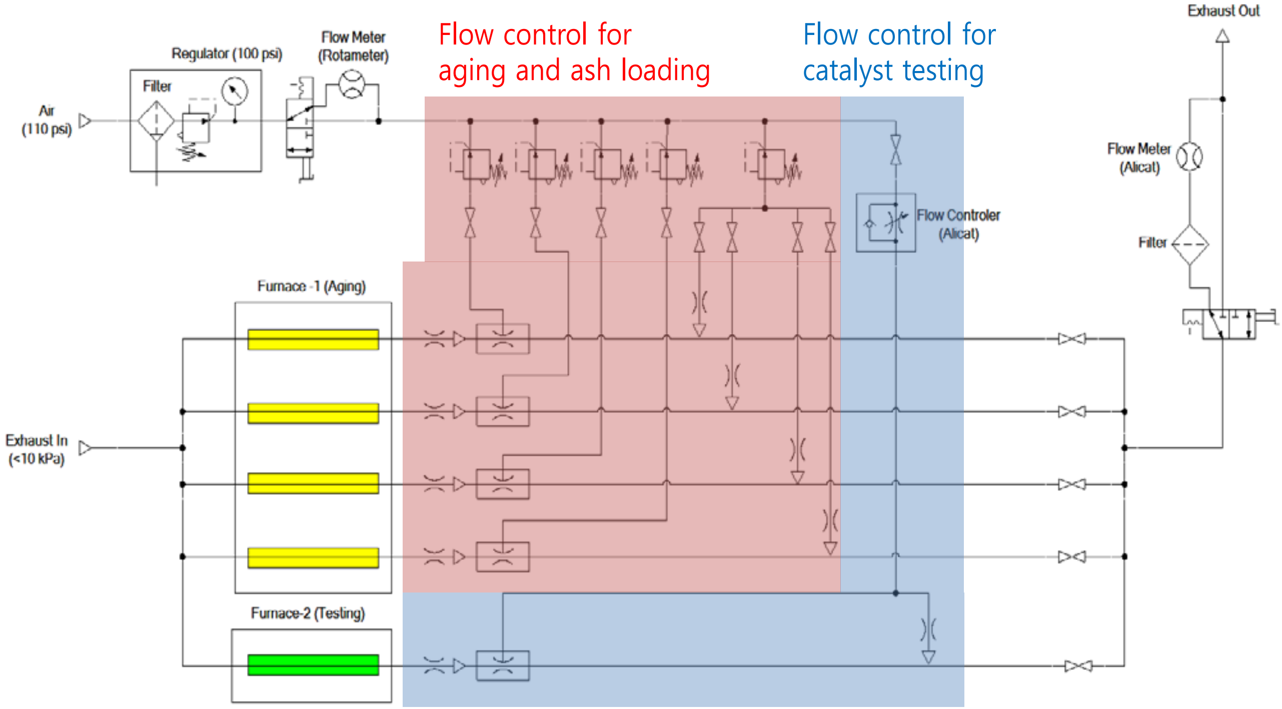


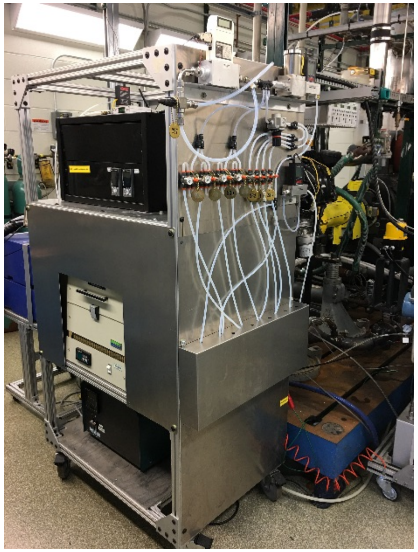
Coated filter



- Size limitation of X-ray tomography at APS has been improved.
  Field of view of 1.5 mm → 5 mm: enabled to analyze filters of four cells
- Porosity variation in bare, coated & aged filters will be examined along the flow path in the next APS beam time.

Flow reactors directly using engine exhaust have been added for better control of exhaust temperatures & kinetics





- Existing set-up has a difficulty in controlling exhaust temperature for ash loading.

→ With the addition of a furnace, controllable temperatures will enable to examine temperature effects on ash loading in filters.

- Time consuming ash loading process for each filter

→ Aging four core filters can enhance experimental cases.

- Kinetic tests will be performed with actual engine exhaust.

Responses to FY16 Reviewer Comments

	Comments	Answer
Approach/ Accomplishment/ Future work	Accelerated oil injection could result in ash loading and ash chemistry different from actual engine drive (like no $CaSO_4$ in rapid aging)	1. We totally agree with this. Despite the reality, Lab-aging is effective at evaluating various samples within a limited timeline. 2. Indeed, $CaSO_4$ exists in ash from field-aged filter. There would be subsequent reactions between ash in filter and SO_2 in exhaust. 3. Ash distribution and morphology will be examined varying exhaust temperature under the new set-up.
Accomplishment	1. Catalyst aging & ash distribution mechanism 2. Convoluted mass transport & kinetic limitations with the flow reactor 3. Indefinite experimental conditions	1. PGM & OSC particle sintering & separation appear to be deactivators ($CePO_4$ is not likely with low P penetration using conventional engine oil. 2. The new set-up enables to examine TWC performance, independent from mass transport & kinetic limitations. 3. Some are intentionally missing with partner's request.
Partner	Catalyst supplier & other partners	TWC coating was serviced from a catalyst company through Hyundai. Will have assistance from ORNL for catalyst characterization.

Collaborations

Collaborating Partners

- *Corning Incorporated*
  - Filter supply & consulting with USA/German staff
- *Hyundai Motor Company*
  - GDI engine and open ECU for full control
  - Technical advice on test results & catalyst coating through a catalyst OEM

Other Internal and Outside Partners

- *Afton Chemical*
  - Collaboration for ash study using experimental oils
- *University of Illinois at Urbana-Champaign*
  - User agreement for XPS and SEM-WDS
- *User Facilities and others at Argonne (Advanced Photon Source & Center for Nanoscale Materials)*
  - STEM-EDS: Dr. Nestor Zaluzec
  - X-ray tomography: Drs. Chris Powell, Alan Kastengren and Katarzyna Matusik
  - XANES: Dr. Sungsik Lee
  - TPR & TPO: Catalyst group in Chemistry Science & Engineering (CSE)

Remaining Challenges and Barriers

- Accelerated aging would not reflect actual ash distribution and ash formation process. Unfortunately field-aged GPFs are difficult to get with high demand under short research history (after discussing with Corning staff).
  - Need to address effects of exhaust temperature, low soot/ash loading

- Despite low/negligible P penetration into wall, reducibility of TWC is noticeable along the path way for the examined field-aged GPF.
  - Temperature effects need to be addressed.
  - Oil-derived particle sintering of active components in TWC is not clear.

Future Work

- Ash loading conditions in the lab-aging reactor to mimic ash distribution in field aged filters
  - Parameters: oil content in fuel, exhaust temperature
  - Ash properties (compactness, chemical compounds) & distribution impacted by these parameters
  - TWC/GPF performance, kinetics
- Continue to propose complete mechanisms of ash formation & TWC/GPF deactivation: from engine oil to ash/gas formation
  - Characterization of lab-aged & field-aged filters – physico-chemical properties
  - Investigation of gaseous P source like H_3PO_4 interacting with TWC and ash compounds

Any future work is subject to change based on funding levels.

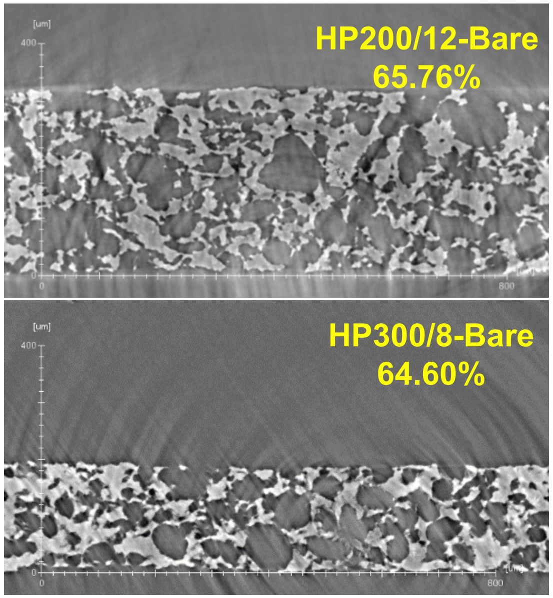
Conclusions

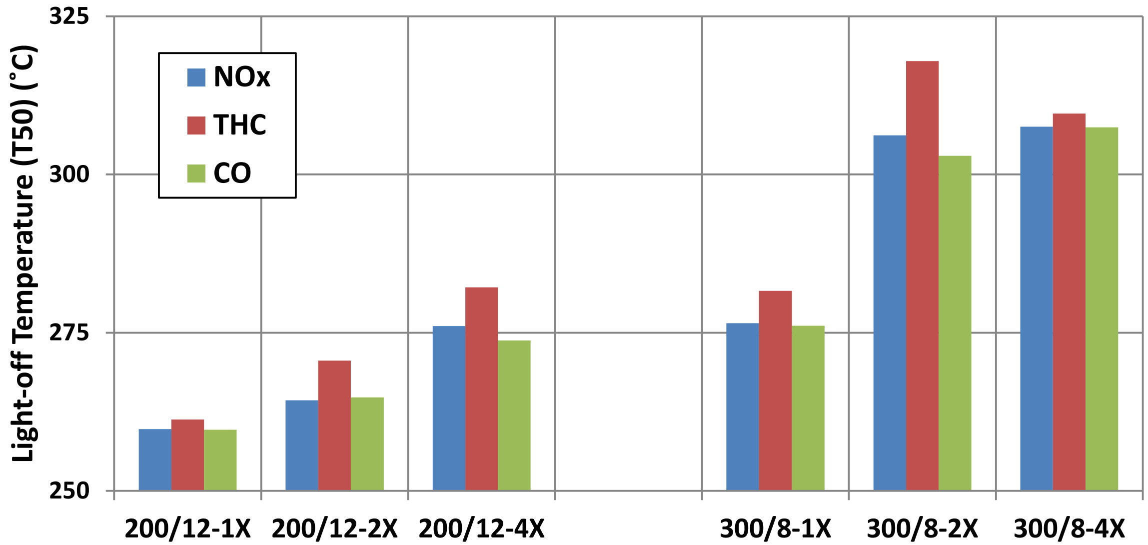
- Lab-aged filters were observed to be deteriorated with ash loading as noted by light-off temperatures, in particular under 300 °C.
- Nox conversion is most apparently impacted even under rich conditions.
- Ash plug significantly increased with 20 g/L, compared with 10 g/L.
- However, ash compactness appears to be low, compared to those of field-aged ash.
- The presence of Ca & P in raw ash particles regardless of engine oil formulation proposes early formation of Ca-P compounds during the combustion process.
- XANES predicts $CaHPO_4$-$2H_2O$, $Ca_5(OH)(PO_4)_2$ & $Zn_3(PO_4)$ as main ash chemicals, although this approach requires further improvement.
- Particle sintering of active components in TWC is detected from TPR.
- Ce reduction is more obvious along the path for the field-aged filter. However, it is not clear if P-CeO_2 interaction is the factor as P penetration is low/negligible.

Technical Back-up

INITIAL TWC PERFORMANCE: BOTH GPF GEOMETRY AND COATING AFFECT LIGHT-OFF OF TWC

Light-off advanced in HP200/12 and lower coating level.





GPF geometry (Bare)

	Geometry	GSA (m²)	Pore Volume (L)
HP200/12	2"X6" (0.3 L)	0.275	0.055
HP300/8		0.345	0.038

Ash loading capacity

TWC coating quality

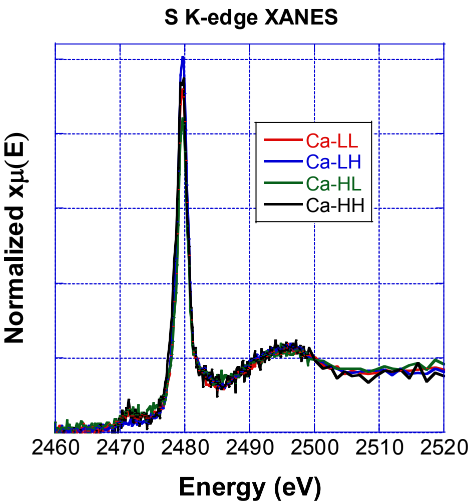
TWC coating specifications

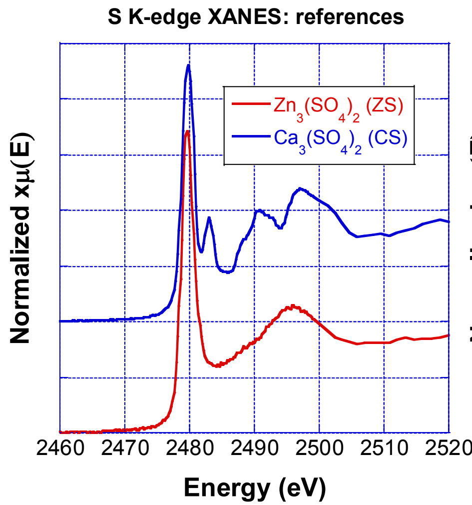
	TWC (g/L) (Support + PGM + OSC)	PGM (g/L)	OSC	PGM concentration in TWC (%)
1X	25	0.5	?	2
2X	50			1
4X	100			0.5

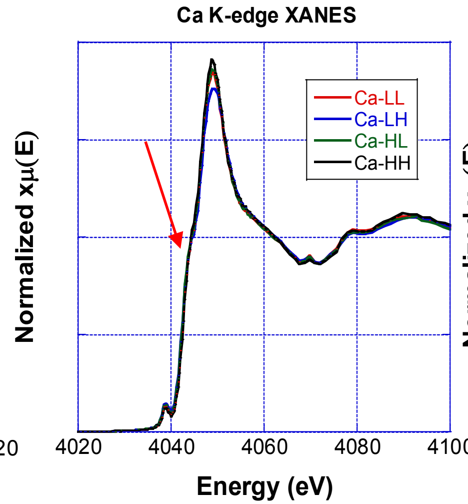
Pore size control: dP, FE

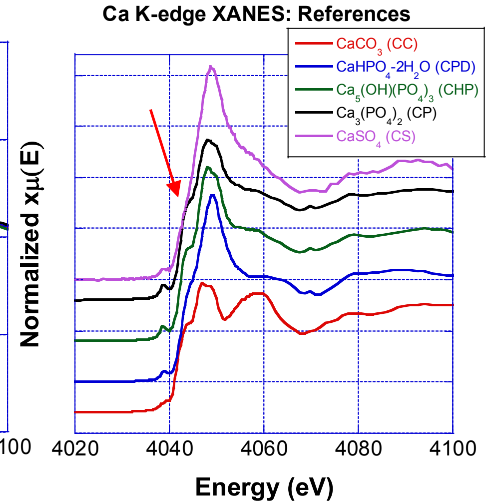
Cost sensitive: fixed

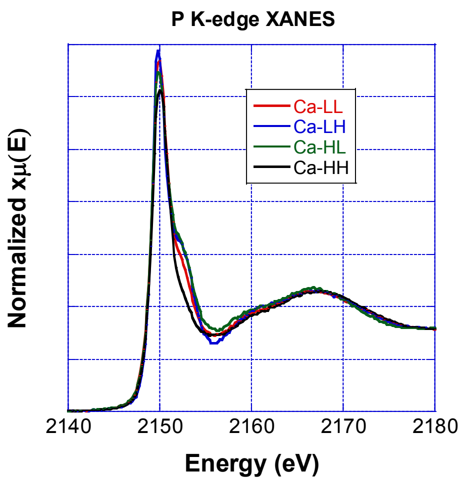
S, Ca & P K-edge XANES Spectra

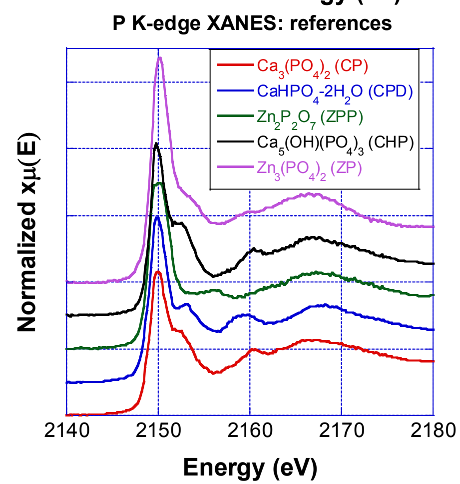










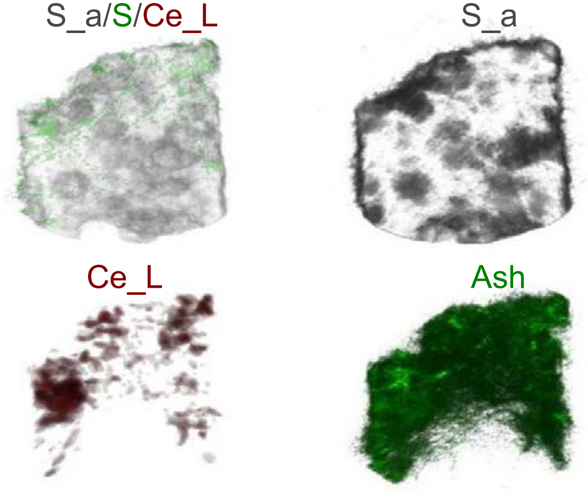


- S & Ca K-edge peak shapes of ash samples appear to be very similar, regardless of oil type, indicating similar ash compounds containing sulfur and calcium.
- S K-edge XANES of ash samples which have much noise due to low concentration are shown to be $Zn_3(PO_4)_2$, suggesting negligible $Ca_3(PO_4)_2$ contribution.
- Low or negligible presence of $CaCO_3$, $Ca_3(PO_4)_2$ & $Zn_2P_2O_7$ (ZDDP antiwear film).

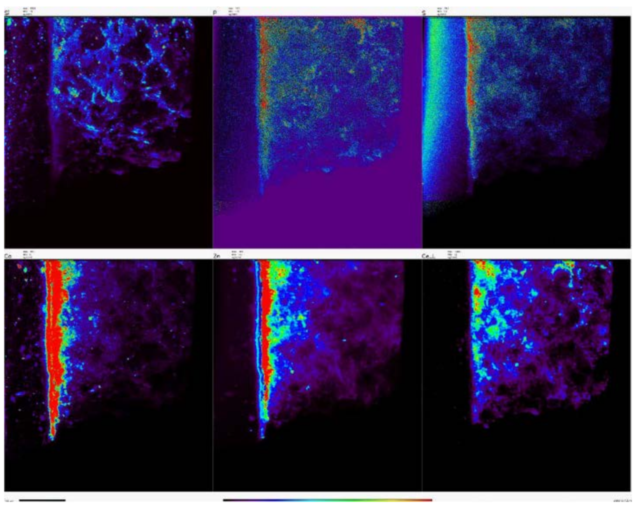
3D XRF tomography was examined with unsuccessful results

- Size limitation (100 µm thickness) made it difficult to prepare samples.
- Zr & P cannot be distinguished in XRF as it has the same detector used in EDS.

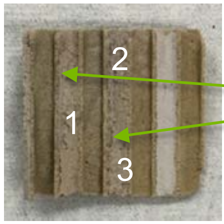
XRF tomography (HP200/12-2X, Ash 10g/L)



2D XRF (HP200/12-2X, Ash 10g/L)

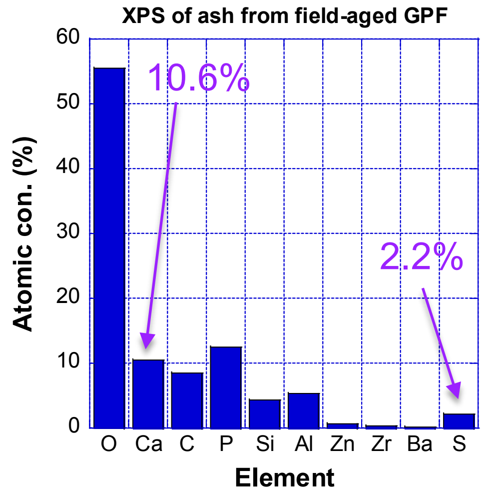


There are significant discrepancies in S content & S compound between ash from field-aged GPF and ash in soot from rapid aging



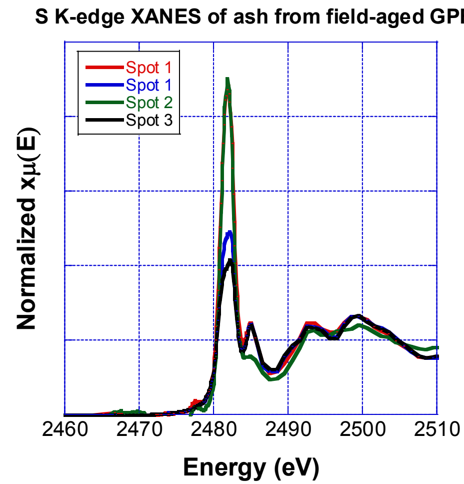
XPS & XANES on ash surfaces

Field-aged GPF (100,000miles)

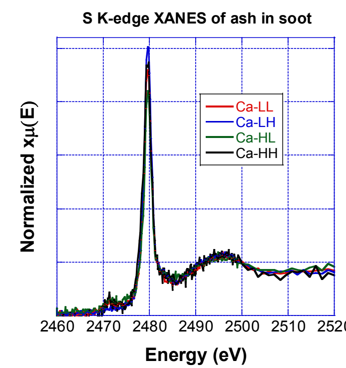


From 2015 AMR

Case	XPS, atomic %				From TGA (mass %)
	Ca	P	Zn	S	
Ca additive	1.23	0	0	0	5.8
P additive	0	2.83	0	0	5.6
ZDDP	0	2.88	0.08	0	16.7



?



- As ash loading in field-aged GPF is low, ash surfaces on the GPF were directly measured using XPS & XANES.
- Ca, P and S contents in ash from field aged GPF are noticeable, while Zn content is low.

\- S content in ash from field-aged GPF is much higher than does that in ash/soot from lab-aging

\- Somehow SAE 2017-01-0930 (Ford) also shows discrepancy in S content between rapid aging and real aging

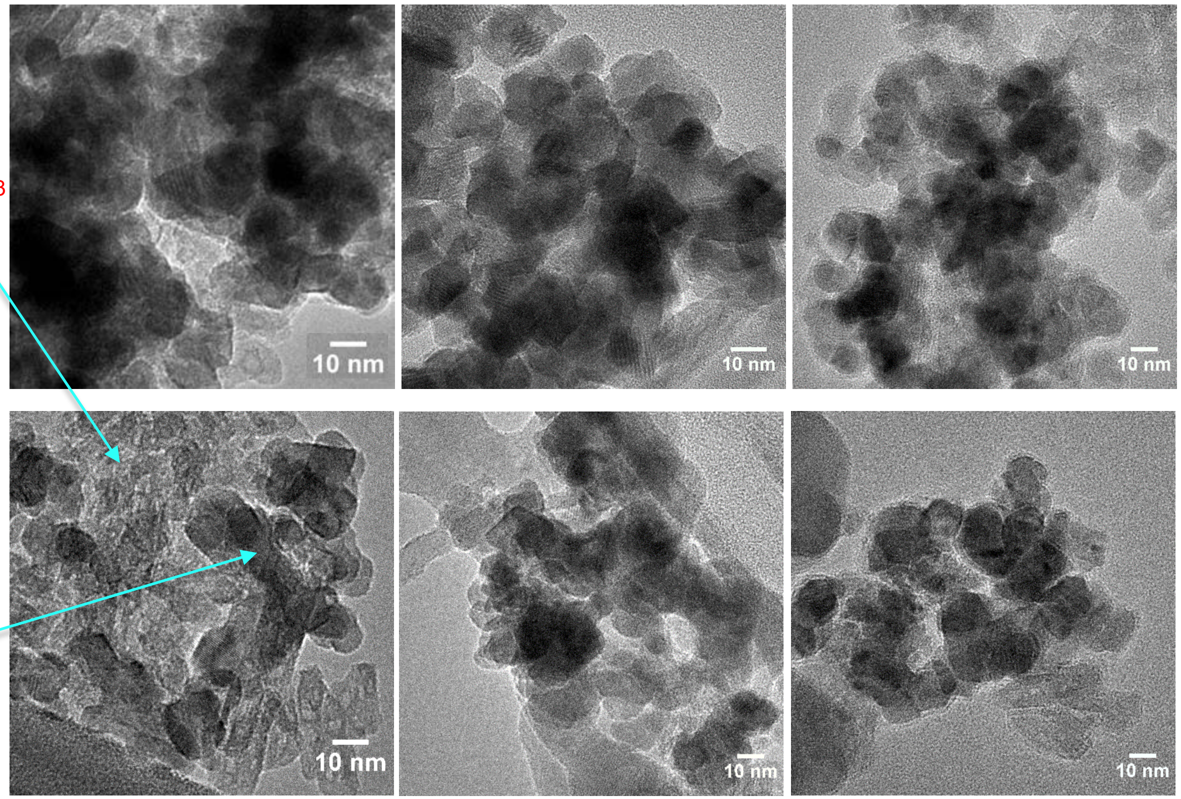
- S K-edge XANES spectra indicate that sulfur compounds are $CaSO_4$ and other types of sulfates, whose result is different from ash in raw soot using rapid aging. High Ca content indicates the presence of other Ca compounds.

\- These results may suggest that ash accumulated on filter reacts with SO_2 over time.

Particle sintering of Pd/Rh is difficult to measure as concentrations in TWC/GPF are low

Fresh TWC/GPF | Lab-aged TWC/GPF | Field-aged TWC/GPF (100,000 miles)

Bright area: Support like Al_2O_3



Dark area: OSC & Pd/Rh

Sample	BET S.A. (m^2/g)
Fresh (200/12-2X)	9.5
Lab-aged (20 g/L ash)	9.3
Field-aged front	10.8
Field-aged mid	8.7
Field-aged rear	7.8

- Extremely low concentration of Pd/Rh in crushed TWC/GPF.
- Size changes with aging were not apparent in the TEM measurements.
- However, BET surface area results hint that catalyst sintering would be significant with aging (in particular, field-aged filter, probably resulted from thermal effects)

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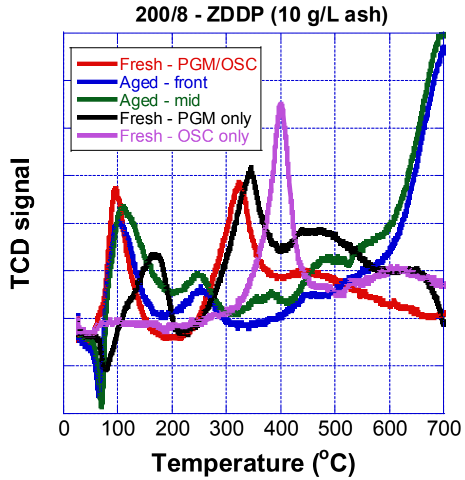
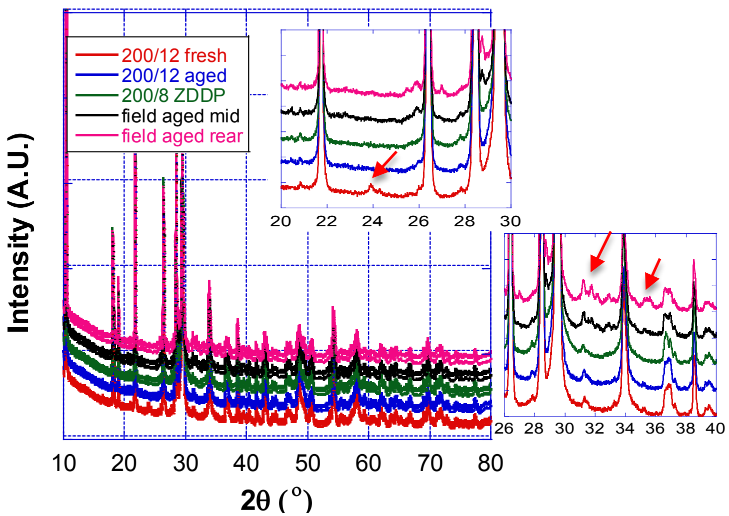
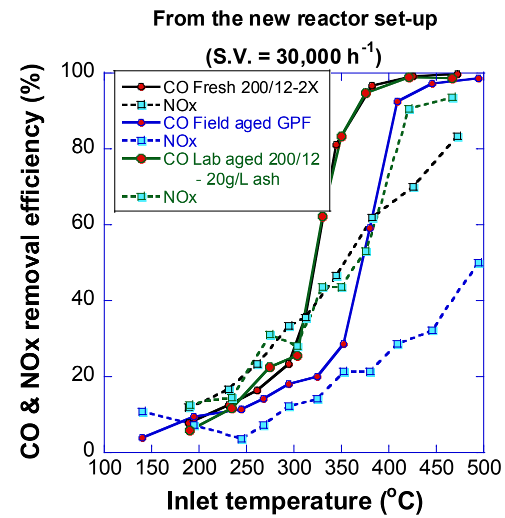
Additional data: TPR, XRD & new reactor test



- From coatings of separate PGM, OSC & PGM/OSC in filters, reducibility of coated filters has been examined.
- OSC helped dispersion of PGM and increased surface oxygen.
- 200 – 400 °C: not only surface oxygen from OSC, but also oxygen available from PGM on alumina
- Bulk oxygen decreased with OSC.





- Due to low concentrations, XRD could not detect major ash compounds like $CaSO_4$, $Ca_3(PO_4)_2$ in lab- & field-aged filters.
- More detail needs to be further analyzed to understand aging impacts (e.g. the peak around 24 o disappeared with aging for lab- & field-aged filters).

- Strangely, the results from the new set-up are not consistent with those from the lab-scale bench reactor → working on uncertainties.
- TWC in the field-aged GPF appears to be much deactivated (unfortunately we don't have its new counterpart to compare with).